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(54) THERMOEXPANSIBLE MICROSPHERE, PROCESS FOR PRODUCING THE SAME AND METHOD OF USE THEREOF

(57) The present invention provides thermo-expansive microspheres comprising thermoplastic resinous shell and a blowing agent, which is a fluorine-containing C_{2-10} compound of ether structure free of chlorine and bromine atoms and gasified at a temperature not higher than the softening point of the thermoplastic resin, being encapsulated in the shell wall; and the production and application processes thereof. The thermo-expansive microspheres have an average particle size ranging from 1 to 100 μm and a coefficient of variation (CV), of particle size distribution being 30 % or less.

The thermo-expansive microspheres have low environmental loading and superior flame-retardation or flame-resistance, and have particle sizes distributing in narrow ranges. Those thermo-expansive microspheres and expanded thermo-expansive microspheres are suitable for applying to fire-proof paints, flame-retardant or flame-resistant thermo-insulating materials, flame-retardant or flame-resistant lightweight fillers, and flame-retardant or flame-resistant lightweight molded products, in addition to the conventional application field.

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Description

Field of Invention

[0001] The present invention relates to thermo-expansive microspheres consisting of thermoplastic resinous shell and a blowing agent encapsulated in the shell, especially to those having superior flame retardation or flame resistance and narrow particle size distribution range; and their production process and application.

Technical Background

[0002] Thermo-expansive microspheres consisting of thermoplastic resinous shell and a blowing agent encapsulated in the shell are generally called thermo-expansive microcapsules. Various processes for producing thermo-expansive microcapsules have been studied. Japanese Patent Publication Sho 42-26524 describes a general process for producing thermo-expansive microcapsules. USP 3615972 describes a production process of thermo-expansive microspheres of which polymeric shell has uniform thickness.

[0003] For producing thermo-expansive microcapsules, hydrocarbons, for example, n-butane, isobutane, isopentane and neopentane, are usually applied. Above all, isobutane and isopentane, which impart superior expanding performance to thermo-expansive microcapsules, are used.

[0004] MATSUMOTO MICROSPHERE (produced by Matsumoto Yushi-Seiyaku Co., Ltd.), a commercially available product of thermo-expansive microcapsules, consists of thermoplastic resin, such as vinylidene chloride polymer, acrylonitrile copolymer and acrylic polymer, in which blowing agents, such as isobutane and isopentane, are encapsulated.

[0005] Thermo-expansive microcapsules produced of polymers containing a high quantity of chloride are flame-retardant even they contain flammable gases. However, they are hazardous because they generate chloride and hydrogen chloride, and further generate phosgene when they are ignited.

[0006] Applying a blowing agent other than flammable hydrocarbons for imparting flame resistance to thermo-expansive microcapsules has been proposed. USP 3615972 discloses certain chlorofluorocarbons applicable for the purpose, though they have not applied in commercial production. Chlorofluorocarbons do not impart sufficient expanding performance to thermo-expansive microcapsules, and they have other shortages.

[0007] Flon has also been applied for various flame-resistant products owing to its special property. Although flon gas was admitted to be inert and have been used for a long time, recently, as popularly known, the use of flon gas has been restricted since the depleting of ozone shield became a serious problem, and applicable fluoro-compounds are being reexamined.

[0008] Actually, chlorofluorocarbon has been replaced by chloride-free aliphatic fluorocarbons or fluorohydrocarbons. Microcapsules produced with those chloride-free fluoro-compounds are disclosed in Japanese Patent Laid Open Hei 6-49260.

[0009] Aliphatic fluorocarbons or fluorohydrocarbons are inert indeed and have low ozone-depleting potential. However, they cannot be applied for producing thermo-expansive microspheres in the form of mixture with hydrocarbons of sufficient quantity for imparting high expanding performance to thermo-expansive microspheres, because their molecules, in which hydrogen of hydrocarbon moiety was only substituted with fluorine, have poor polarity and compatibility to hydrocarbons. Application of only one aliphatic fluorocarbon or fluorohydrocarbon causes a serious problem, i.e., insufficient expanding performance of microspheres, because such fluorocarbon cannot be completely encapsulated in thermoplastic resinous shell in polymerization reaction due to their poor compatibility to monomers, and results in the formation of microspheres of which thermo-plastic resinous shell is impregnated with the fluorocarbon.

[0010] PCT International Application nationalized and published in Japan No. 2002-511900 discloses thermo-expansive hollow particles, of which hollow is filled with an expanding agent of the mixture of (a) fluoro-hydrocarbon fluid and (b) organic ester, ether or ketone. Although fluoro-hydrocarbon fluids, such as aliphatic fluorocarbons or fluorohydrocarbons, are inert and have low ozone-depleting potential as described above, they are not preferable because of their high global warming potential. Aliphatic fluorocarbons or fluorohydrocarbons with low fluorine-substitution degree are not preferable, even if they are compatible to monomers, because resultant thermo-expansive hollow particles exhibit flammability. The particle sizes of the thermo-expansive hollow particles produced with those fluorine compounds distribute in a broad range, for example, a distribution range with 30 % or more of CV, coefficient of variation, and thus those fluorocarbons cause difficulty in providing products of constant expanding performance.

[0011] In the examples 11 and 12 of the nationalized and published patent application, thermo-expansive hollow particles produced with the mixture of 1,1,1,2,3,4,4,5,5,5-decafluoropentane and perfluorohexane (PF-5060) as (a) fluorohydrocarbon fluid, and with dimethyl hexafluoroglutarate or dimethyl octafluoroadipate as (b) organic ester, ether or ketone to be admixed are described as examples. The hollow particles have low expanding capacity and their particle size distributes in a broad range.

[0012] With those reasons, expansive microcapsules are not commercially available at present.

Disclosure of Invention

[0013] The object of the present invention is to provide thermo-expansive microspheres having low environmental loading, superior flame-resistance or flame-retardation, and particle sizes distributing in narrow range.

[0014] Another object of the present invention is to provide expanded hollow microspheres of spherical shape having particle sizes distributing in narrow range and low specific gravity.

[0015] Further object of the present invention is to provide thermo-expansive microspheres and expanded hollow microspheres applicable to flame-retardant or flame-resistant thermo-insulating materials, flame-retardant or flame-resistant light-weight fillers, and flame-retardant or flame-resistant light-weight molded products.

[0016] Further object of,the present invention is to provide a production process of the thermo-expansive microspheres of the present invention, which have the performances mentioned above.

[0017] Further object of the present invention is to provide compositions containing the thermo-expansive microspheres or expanded hollow microspheres of the present invention.

[0018] Further object and advantages of the present invention are clearly illustrated in the following description.

[0019] According to the present invention, the objects and advantages of the present invention described above are attained, first, with thermo-expansive microspheres, which are characterized by thermoplastic resinous shell and a blowing agent encapsulated in the shell, wherein the blowing agent is a fluorine-containing C_{2-10} compound of ether structure free of chlorine and bromine atoms, and gasified at a temperature below the softening point of the thermoplastic resin.

[0020] According to the present invention, the objects and advantages of the present invention described above are attained, second, with expanded hollow microspheres, which are characterized by their production process wherein thermo-expansive microspheres of the present invention are heated at a temperature above the softening point of the thermoplastic resinous shell to be expanded with 10 or more of coefficient of expansion and produced into expanded microspheres having a true specific gravity of 0.1 g/cc or less and a particle size distribution with 30 % or lower coefficient of variation.

[0021] According to the present invention, the objects and advantages of the present invention described above are attained, third, with the production process of thermo-expansive microspheres, which are characterized by polymerizing at least one polymerizable monomer in an aqueous dispersion in the presence of a blowing agent to produce thermo-expansive microspheres, wherein the blowing agent is a fluorine-containing C_{2-10} compound of ether structure free of chlorine and bromine atoms.

Best Mode of Embodiment

[0022] The thermo-expansive microspheres of the present invention contain a fluorine-containing C_{2-10} compound of ether structure free of chlorine and bromine atoms as a blowing agent. Fluorine-containing compounds gasifying at a temperature below the softening point of thermoplastic resinous shell of thermo-expansive microspheres are preferable. For example, hydrofluoroethers, such as $C_3F_7OCH_3$, $C_4F_9OCH_3$, $C_4F_9OC_2H_5$, and $C_7F_{15}OC_2H_5$, are preferable, though the blowing agents are not restricted within the scope of those examples. The alkyl groups of the hydrofluoroether may be either linear or branched. The amount of the blowing agent described above preferably ranges from 2.0 to 85.0 weight percent of thermo-expansive microspheres, more preferably from 10.0 to 60.0 weight percent, and the most preferably from 15.0 to 50.0 weight percent.

[0023] In addition to composing the whole of a blowing agent with fluorine compounds, other compounds, which are usually applied as blowing agents and gasify at a temperature below the softening point of the thermoplastic resinous shell of thermo-expansive microspheres, can be admixed.

[0024] The examples of those compounds are halogenides of propane, propylene, butene, normal butane, isobutane, isopentane, neopentane, normal pentane, normal hexane, isohexane, heptane, octane, petroleum ether and methane; low-boiling-point fluids, such as tetraalkyl silane; and azodicarbonamide, which thermally decomposes and gasifies. Those compounds are selected according to the temperature range where thermo-expansive microspheres are intended to be expanded. For reflecting the property of fluorine compounds to thermo-expansive microspheres, it is preferable to control the ratio of blowing agents other than fluorine-containing compounds into 50 weight percent or less of the whole of blowing agents employed. Greater ratio of fluorine-containing compounds in the whole of a blowing agent results in higher reflection of the property of fluorine-containing compounds to thermo-expansive microspheres, and thus enables to provide flame-retardant or flame-resistant thermo-expansive microcapsules.

[0025] The thermoplastic resins for forming the shell of the thermo-expansive microspheres of the present invention are comprised of the polymer of radically polymerizable monomers. The examples of those monomers are nitrile monomers, such as acrylonitrile, methacrylonitrile, α-chloro acrylonitrile, α-ethoxy acrylonitrile, and fumaronitrile; carboxylic acid monomers, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, and citraconic acid; vinylidene chloride; vinyl acetate; (meth)acrylates, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)

acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, isobornyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, and β-carboxyethyl acrylate; styrene monomers, such as styrene, α-methyl styrene, and chlorostyrene; amide monomers, such as acrylamide, substituted acrylamide, methacrylamide, and substituted methacrylamide; and optional mixture thereof. Thermo-expansive microspheres having superior heat resistance are those having shell of thermoplastic resin produced from nitrile monomers. The mixture of acrylonitrile and methacrylonitrile is especially preferable. The ratio of nitrile monomers is preferably 80 weight percent or more, more preferably 90 weight percent or more. Shell consisting of less than 80 weight percent of nitrile monomers is not preferable for heat-resistant thermo-expansive microspheres.

[0026] The examples of cross-linking agents or polymerizable monomers having two or more of polymerizable double bonds to be added to the monomers described above within the scope of the present invention are listed below: For example, aromatic divinyl compounds, such as divinyl benzene and divinyl naphthalene; aryl methacrylate, triacrylformal, triallyl isocyanate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth) acrylate, 1,4-butanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, PEG (200) di(meth)acrylate, PEG (400) di(meth)acrylate, PEG (600) di(meth)acrylate, neopentylglycol di(meth)acrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, trimethylolpropane trimethacrylate, glycerin dimethacrylate, dimethylol tricyclodecane diacrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetraacrylate, dipentaerythritol hexaacrylate, neopentylglycol acrylic acid benzoate, trimethylolpropane acrylic acid benzoate, 2-hydorxy-3-acryloyloxypropylmethacrylate, hydroxypivalic acid neopentylglycol diacrylate, ditrimethylolpropane tetraacrylate, and 2-butyl-2-ethyl-1,3-propanediol diacrylate; and the mixture thereof. The amount of those cross-linking agents ranges preferably from 0.01 to 5 weight percent, more preferably from 0.05 to 3 weight percent. An amount less than 0.01 weight percent is not preferable because it results in low degree of cross-linking which leads to poor retention of encapsulated blowing agent and poor heat resistance of resultant microspheres. An amount greater than 5 weight percent is not preferable because it results in excessive degree of cross-linking which extremely deteriorates the expanding performance of microspheres.

[0027] Shell materials for thermo-expansive microspheres are prepared by adding proper polymerization initiators to the components described above. Polymerization initiators, such as peroxides and azo compounds, which are known to those skilled in the art, can be employed. The examples of those polymerization initiators are peroxides, such as azobisisobutyronitrile, benzoyl peroxide, lauryl peroxide, diisopropyl peroxidicarbonate, and t-butyl peroxide; and azo compounds, such as 2,2'-azobis (4-methoxy-2,4-dimethyl valeronitrile), 2,2'-azobis isobutyronitrile, 2,2'-azobis (2,4-dimethyl valeronitrile), 2,2'-azobis (2-methyl propionate), and 2,2'-azobis (2-methyl) butyronitrile. Preferable polymerization initiators are oil-soluble initiators which are soluble in polymerizable monomers employed.

[0028] For producing thermo-expansive microspheres, conventional processes for producing thermo-expansive microcapsules are usually employed. In those processes, inorganic microparticles such as colloidal silica, colloidal calcium carbonate, magnesium hydroxide, calcium phosphate, aluminum hydroxide and alumina, are employed as the stabilizers for aqueous dispersion. In addition, polymeric auxiliaries for those dispersion stabilizers, such as the condensation products of diethanolamine and aliphatic dicarboxylic acid, polyvinyl pyrolidone, methyl cellulose, polyethylene oxide and polyvinyl alcohol; cationic surfactants, such as alkyltrimethyl ammonium chloride and dialkyldimethylammonium chloride; anionic surfactants, such as sodium alkyl sulfate; amphoteric surfactants, such as alkyldimethyl aminoacetic acid betaine and alkyldihydroxyethyl aminoacetic acid betaine; and various emulsifiers are employed as the auxiliaries for dispersion stabilizers.

[0029] The preferable thermo-expansive microspheres of the present invention have average particle sizes ranging from 1 to 100 μm and particle size distribution with 30 % or less of coefficient of variation (CV). The average particle size of the thermo-expansive microcapsules of the present invention can be controlled in a broad range and designed freely according to their end uses. The coefficient of variation (CV), is calculated by the following formula:

$$CV = (S / < X >) \times 100 \, (\%) \qquad (1)$$

$$S = \{ \textstyle\sum_{i=1}^{n} (Xi - < X >)^2 / (n - 1) \}^{1/2} \qquad (2)$$

wherein S is the standard deviation of particle size, <X> is an average particle size, Xi is the size of a particle in the i-th order, and n is the number of particles.

[0030] For producing expanded hollow microspheres from the thermo-expansive microspheres of the present invention, it is preferable to heat the microspheres at a temperature not lower than the softening point of the thermoplastic resin of the shell to expand the microspheres to a volume which is ten times or more of their original volume. With this treatment, expanded hollow microspheres having a true specific gravity of 0.1 g/cc or lower and particle size distribution

with 30 % or lower coefficient of variation (CV) are produced. A coefficient of variation (CV) of particle size distribution greater than 30 % is not preferable because it means that thermo-expansive microspheres have variable expanding performance. Such thermo-expansive microspheres will adversely affect on the surface finish of products in which the thermo-expansive microspheres are blended or mixed.

[0031] The average particle sizes of the thermo-expansive microspheres and expanded hollow microspheres of the present invention were determined by a laser diffraction particle size distribution tester (Heros & Rodos, manufactured by Sympatec Co., Ltd.).

[0032] The true specific, gravity of the thermo-expansive microcapsules of the present invention was determined by a liquid substitution method with isopropyl alcohol.

[0033] The expansion coefficient of thermo-expansive microspheres was determined by dividing the true specific gravity of the unexpanded thermo-expansive microspheres with the true specific gravity of expanded hollow microspheres, which was measured by heating the thermo-expansive microspheres in a Perfect Oven manufactured by Tabai Espec Co., Ltd. at a certain temperature (expanding temperature) for two minutes.

[0034] Fine-particle fillers for the thermo-expansive microspheres of the present invention, which has smaller particle sizes than the thermo-expansive microspheres, preferably of which primary particle sizes are smaller than one tenth of the particle size of the thermo-expansive microspheres, are selected among organic fillers or inorganic fillers according to the purpose of their use, such as improving dispersibility in materials or flowability of microspheres. The preferable ratio of the fine-particle fillers to thermo-expansive microspheres ranges from 0.1 to 95 weight percent, more preferably from 0.5 to 60 weight percent, and most preferably from 5 to 50 weight percent.

[0035] The examples of the organic fillers are metal soaps, such as magnesium stearate, calcium stearate, zinc stearate, barium stearate, and lithium stearate; resin powders, such as polytetrafluoroethylene beads and polymethyl methacrylate beads; and polyamide fiber.

[0036] The examples of the inorganic fillers are silica, alumina, mica, talc, isinglass, calcium carbonate, calcium hydroxide, calcium phosphate, magnesium hydroxide, magnesium phosphate, barium sulfate, titanium dioxide, zinc oxide, ceramic beads, glass beads, crystal beads, carbon black, and molybdenum disulfide. Those organic or inorganic fillers can be used in a form of mixture.

[0037] Ordinary powder mixers, which can oscillate and agitate powder, are employed for mixing thermo-expansive microcapsules and fine-particle fillers. Specifically, powder mixers which can oscillate and agitate or agitate powder, such as ribbon-type mixers and vertical screw mixers, can be employed. Recently, highly efficient multi-functional powder mixers manufactured by combining several agitation devices, such as Super Mixer (manufactured by Kawata MFG Co. , Ltd.), High-Speed Mixer (manufactured by Fukae Co., Ltd.) and New-Gram Machine (manufactured by Seishin Enterprise Co., Ltd.), have been introduced and thus they are employable. In addition, a simple device consisting of a vessel and paddle blades is applicable.

[0038] The said fine-particle fillers stick on the surface of thermo-expansive microspheres.

[0039] The thermo-expansive microspheres of the present invention can be processed into lightweight foamed compositions by blending with resins, such as rubber, thermoplastic resins, and thermo-setting resins, and by heating.

[0040] Expanded hollow microspheres produced from the thermoplastic microspheres of the present invention can be processed into lightweight resin compositions by blending with resins, such as rubber, thermoplastic resins, and thermo-setting resins. The examples of applicable resins are SBS (styrene-butadiene-styrene block copolymer), PVC (polyvinyl chloride), PP (polypropylene), PE (polyethylene), PU (polyurethane), PS (polystyrene), natural rubber, acrylic resin, epoxy resin, and silicone resin, though the applicable resins are not restricted within the scope of those examples.

[0041] The preferable ratio of thermo-plastic microspheres and expanded hollow microspheres in a resultant composition ranges from 0.5 to 50 weight percent, more preferably from 1.0 to 30 weight percent.

[0042] The advantages of the thermo-expansive microspheres of the present invention are processability into expanded hollow microspheres with almost no emission of fluorine-containing compounds; much narrower particle size distribution range than the ranges of other thermo-expansive microspheres in which aliphatic fluorocarbons or fluoro hydrocarbons are encapsulated; and superior expanding performance. Another advantage of the thermo-expansive microspheres in which such blowing agents are encapsulated is their applicability as flame-retardant or flame-resistant materials having low environmental loading.

[0043] The thermo-expansive microspheres and expanded hollow microspheres of the present invention are applicable to various end uses. Unexpanded thermo-expansive microspheres are applied as the fillers for automobile paints and the foaming agents for foaming inks applied to wall papers and decoration for apparels owing to their thermo-expansive performance. Furthermore, unexpanded thermo-expansive microspheres can be used as foaming agents for imparting lightweight, porous, cushioning and thermo-insulating property in a process where the microspheres are blended with thermoplastic resins or thermo-setting resins and heated to expand the microspheres at a temperature higher than a point at which the microspheres start to expand.

[0044] Expanded thermo-expansive microspheres can be applied as lightweight fillers for paints, putty, composite materials, paper, and insulating materials, and as volume-retaining materials for pressure vessels, owing to their low

density and filling effect. As described above, the thermo-expansive microspheres of the present invention can be applied to the same end uses as those for conventional thermo-expansive microspheres.

[0045] Further, the present invention can be applied to flame-resistant paints and insulating materials. In flame-resistant paints, the above-mentioned thermo-expansive microspheres can be used as flame-retardent or flame-resistant fillers.

Examples

[0046] The present invention is described precisely with the following examples and comparative examples.

Example 1

[0047] A water phase was prepared by adding 150 g of salt water, 3.0 g of an adipic acid-diethanolamine condensate, and 20 g of colloidal silica (20 % concentration) in 500 g of deionized water and by homogenizing the mixture with agitation.

[0048] An oil phase was prepared by mixing 200 g of acrylonitrile, 70 g of methacrylonitrile, 5.0 g of methyl methacrylate, 1.2 g of ethylene glycol dimethacrylate, 2.0 g of azobisisobutyronitrile, and 150 g of methylperfluorobutyl ether, and by dissolving the components with agitation.

[0049] Then the water phase and oil phase were mixed preliminarily with a homogenizer at 3,000 rpm for 2 minutes, and then agitated at 10,000 rpm for 2 minutes to be prepared into suspension. Then the suspension was transferred in a reactor, purged with nitrogen, and reacted at 61°C for 20 hours under agitation. The reaction product was filtered and dried. The resultant microspheres had the average particle size of 30 μm with the Coefficient of variation (CV) of 27 %. The true specific gravity of the thermo-expansive microspheres was determined to be 1.23 g/cc. The ratio of the volatile matter in the expanding agent encapsulated in the thermo-expansive microspheres was determined to be 33.8 weight percent. A source of ignition was brought close to the thermo-expansive microspheres, but they did not burn. The angle of repose of the microspheres, which indicates the degree of flowability of powder, was determined with a Powder Tester (PT-N, manufactured by Hosokawa Micron Corporation), and the result was 43 degrees.

[0050] The resultant thermo-expansive microspheres were heated at 160 °C for 2 minutes to be processed into expanded hollow microspheres. The expanded hollow microspheres had the average diameter of 120 μm with the Coefficient of variation (CV) of 27 %. The true specific gravity of the microspheres was 0.020 g/cc, with the expansion coefficient of 61. Subsequently the ratio of volatile matter in the blowing agent encapsulated in the expanded hollow microspheres was determined and the result was 33.2 weight percent. The expanded hollow microspheres did not burn when a source of ignition was brought close to them.

Example 2

[0051] The thermo-expansive microspheres produced in Example 1 and titanium dioxide, having the average particle size of 15 nm, were mixed in 6:4 weight ratio and agitated uniformly with a Super Mixer (manufactured by Kawata MFG Co., Ltd.) to produce thermo-expansive microspheres of which surface was coated with titanium dioxide. Their average particle size was 30 μm with the coefficient of variation (CV) of 27 %. The angle of repose of the microspheres was determined to be 0 degree, exhibiting excellent flowability.

Example 3

[0052] Thermo-expansive microspheres were produced in the same manner as in Example 1 except that an inline homogenizer was employed instead of the homogenizer. The resultant thermo-expansive microspheres had the average particle size of 31 μm with the coefficient of variation (CV) of 15 %, and the true specific gravity of 1.20 g/cc, and the blowing agent contained 33.2 weight percent of volatile matter. The thermo-expansive microspheres did not burn when a source of ignition was brought close to them.

[0053] The microspheres were heated at 160 °C for 2 minutes in the same manner as in Example 1 to be processed into expanded hollow microspheres. The expanded hollow microspheres had the average particle size of 120 μm with the coefficient of variation (CV) of 16 %, the true specific gravity of 0.021 g/cc, and the expansion coefficient of 57.

[0054] Subsequently the ratio of the volatile matter in the blowing agent encapsulated in the expanded hollow microspheres was determined and the result was 31.9 weight percent. The expanded hollow microspheres did not burn when a source of ignition was brought close to them.

Comparative Example 1

[0055] Thermo-expansive microspheres were produced in the same manner as in Example 1 except that 150 g of methylperfluorobutyl ether was replaced by 65 g of isohexane.
[0056] The resultant thermo-expansive microspheres had the average particle size of 31 μm with the coefficient of variation (CV) of 44 %, and the true specific gravity of 1.02 g/cc, and the blowing agent contained 17.5 weight percent of volatile matter. The thermo-expansive microspheres inflamed when a source of ignition was brought close to them.
[0057] The microspheres were heated at 160 °C for 2 minutes in the same manner as in Example 1 to be processed into expanded hollow microspheres. The expanded hollow microspheres had the average particle size of 110 μm with the coefficient of variation (CV) of 42 %, the true specific gravity of 0.019 g/cc, and the expansion coefficient of 53.
[0058] Subsequently the ratio of the volatile matter in the blowing agent encapsulated in the expanded hollow microspheres was determined, and the result was 14.6 weight percent. The expanded hollow microspheres inflamed when a source of ignition was brought close to them.

Comparative Example 2

[0059] Thermo-expansive microspheres were produced in the same manner as in Example 1 except that 150 g of methylperfluorobutyl ether was replaced by 181.5 g of perfluorocarbon (C_6F_{14}).
[0060] The resultant thermo-expansive microspheres had the average particle size of 30 μm with the coefficient of variation (CV) of 45 %, and the true specific gravity of 1.20 g/cc, and the blowing agent contained 22.5 weight percent of volatile matter. The thermo-expansive microspheres did not burn when a source of ignition was brought close to them.
[0061] The microspheres were heated at 160 °C for 2 minutes in the same manner as in Example 1 to be processed into expanded hollow microspheres. The expanded hollow microspheres had the average particle size of 110 μm with coefficient of variation (CV) of 46 %, the true specific gravity of 0.028 g/cc, and the expansion coefficient of 43.
[0062] Subsequently the ratio of the volatile matter in the blowing agent encapsulated in the expanded hollow microspheres was determined, and the result was 24.3 weight percent. The expanded hollow microspheres did not burn when a source of ignition was brought close to them.

Comparative Example 3

[0063] Thermo-expansive microspheres were produced in the same manner as in Comparative Example 2 except that 7.0 g of dimethyl adipate was added to the oil phase.
[0064] The resultant thermo-expansive microspheres had the average particle size of 21 μm with the coefficient of variation (CV) of 48 %, and the true specific gravity of 1.19 g/cc, and the blowing agent contained 20.5 weight percent of volatile matter. The thermo-expansive microspheres did not burn when a source of ignition was brought close to them.
[0065] The microspheres were heated at 160 °C for 2 minutes in the same manner as in Example 1 to be processed into expanded hollow microspheres. The expanded hollow microspheres had the average particle size of 70 μm with the coefficient of variation (CV) of 48 %, the true specific gravity of 0.032 g/cc, and the expansion coefficient of 37.
[0066] Subsequently the ratio of the volatile matter in the blowing agent encapsulated in the expanded hollow microspheres was determined, and the result was 16.3 weight percent. The expanded hollow microspheres did not burn when a source of ignition was brought close to them.

Comparative Example 4

[0067] Thermo-expansive microspheres were produced in the same manner as in Comparative Example 3 except that 7.0 g of dimethyl adipate in the oil phase was replaced by 12.7 g of dimethyl octafluoroadipate.
[0068] The resultant thermo-expansive microspheres had the average particle size of 18 μm with the coefficient of variation (CV) of 42 %, and the true specific gravity of 1.21 g/cc, and the blowing agent contained 24.5 weight percent of volatile matter. The thermo-expansive microspheres did not burn when a source of ignition was brought close to them.
[0069] The microspheres were heated at 160 °C for 2 minutes in the same manner as in Example 1 to be processed into expanded hollow microspheres. The expanded hollow microspheres had the average particle size of 38 μm with the coefficient of variation (CV) of 41 %, the true specific gravity of 0.172 g/cc, and the expansion coefficient of 7.
[0070] Subsequently the ratio of the volatile matter in the blowing agent encapsulated in the expanded hollow microspheres was determined, and the result was 16.5 weight percent. The expanded hollow microspheres did not burn when a source of ignition was brought close to them.

Example 4

[0071] Thermo-expansive microspheres were produced in the same manner as in Example 1 except that the oil phase was prepared by mixing 200 g of acrylonitrile, 75 g of methyl methacrylate, 1.2 g of ethyleneglycol dimethacrylate, 2.0 g of azobisisobutyronitrile, 100 g of methylperfluorobutyl ether, and 20 g of isobutane, and agitating to dissolve those components.

[0072] The resultant thermo-expansive microspheres had the average particle size of 22 μm with the coefficient of variation (CV) of 25 %, and the true specific gravity of 1.15 g/cc, and the blowing agent contained 28.9 weight percent of volatile matter. The thermo-expansive microspheres did not burn when a source of ignition was brought close to them.

[0073] The microspheres were heated at 140 °C for 2 minutes to be processed into expanded hollow microspheres. The expanded hollow microspheres had the average particle size of 88 μm with the coefficient of variation (CV) of 24 %, the true specific gravity of 0.019 g/cc, and the expansion coefficient of 63.

[0074] Subsequently the ratio of the volatile matter in the blowing agent encapsulated in the expanded hollow microspheres was determined, and the result was 26.3 weight percent. The expanded hollow microspheres did not burn when a source of ignition was brought close to them.

Comparative Example 5

[0075] Thermo-expansive microspheres were produced in the same manner as in Example 4, except that 100 g of methylperfluorobutyl ether was replaced by 41.0 g of isohexane.

[0076] The resultant thermo-expansive microspheres had the average particle size of 21 μm with the coefficient of variation (CV) of 38 %, and the true specific gravity of 1.03 g/cc, and the blowing agent contained 15.2 weight percent of volatile matter. The thermo-expansive microspheres inflamed when a source of ignition was brought close to them.

[0077] The microspheres produced in the same manner in Example 4 were heated at 140 °C for 2 minutes to be processed into expanded hollow microspheres. The expanded hollow microspheres had the average particle size of 76 μm with the coefficient of variation (CV) of 39 %, the true specific gravity of 0.021 g/cc, and the expansion coefficient of 49.

[0078] Subsequently the ratio of the volatile matter in the blowing agent encapsulated in the expanded hollow microspheres was determined, and the result was 11.3 weight percent. The expanded hollow microspheres inflamed when a source of ignition was brought close to them.

Example 5

[0079] Thermo-expansive microspheres were produced in the same manner as in Example 1 except that the oil phase was prepared by mixing 150 g of acrylonitrile, 120 g of vinylidene chloride, 5.0 g of methyl methacrylate, 0.8 g of trimethylolpropane trimethacrylate, 1.0 g of diisopropyl peroxidicarbonate, 90 g of methylperfluorobutyl ether, and 20 g of isobutane, and agitating to dissolve those components.

[0080] The resultant thermo-expansive microspheres had the average particle size of 15 μm with the coefficient of variation (CV) of 24 %, and the true specific gravity of 1.33 g/cc, and the blowing agent contained 25.9 weight percent of volatile matter. The thermo-expansive microspheres did not burn when a source of ignition was brought close to them.

[0081] The microspheres were heated at 120 °C for 2 minutes to be processed into expanded hollow microspheres. The expanded hollow microspheres had the average particle size of 63 μm with the coefficient of variation (CV) of 24 %, the true specific gravity of 0.018 g/cc, and the expansion coefficient of 72.

[0082] Subsequently the ratio of the volatile matter in the blowing agent encapsulated in the expanded hollow microspheres was determined, and the result was 24.7 weight percent. The expanded hollow microspheres did not burn when a source of ignition was brought close to them.

Comparative Example 6

[0083] Thermo-expansive microspheres were produced in the same manner as in Example 3, except that 90 g of methylperfluorobutyl ether was replaced by 38.9 g of normal pentane.

[0084] The resultant thermo-expansive microspheres had the average particle size of 13 μm with the coefficient of variation (CV) of 38 %, and the true specific gravity of 1.26 g/cc, and the blowing agent contained 14.2 weight percent of volatile matter. The thermo-expansive microspheres inflamed when a source of ignition was brought close to them.

[0085] The microspheres were heated at 120 °C for 2 minutes in the same manner as in Example 5 to be processed into expanded hollow microspheres. The expanded hollow microspheres had the average particle size of 46.4 μm with the coefficient of variation (CV) of 39 %, the true specific gravity of 0.029 g/cc, and the expansion coefficient of 43.

[0086] Subsequently the ratio of the volatile matter in the blowing agent encapsulated in the expanded hollow mi-

crospheres was determined, and the result was 9.3 weight percent. The expanded hollow microspheres inflamed when a source of ignition was brought close to them.

Example 6

[0087] Two weight percent of the thermo-expansive microspheres produced in Example 1 was moistened with 2 weight percent of a process oil, mixed with 96 weight percent of SBS (styrene-butadiene-styrene block copolymer, having the specific gravity of 0.9 g/cm^3), and knead with biaxial rolls at 80 °C to be processed into rubber sheet. Then the rubber sheet was heated at 150 °C for 10 minutes with a hot pressing device to be processed into foamed rubber sheet. The result is shown in Table 1.

Comparative Example 7

[0088] Foamed rubber sheet was produced in the same manner as in Example 6, except that the thermo-expansive microspheres produced in Comparative Example 4 was employed instead of the thermo-expansive microspheres produced in Example 1. The result is shown in Table 1.

Table 1

	Surface finish of foamed rubber sheet (*1)	Specific gravity of foamed rubber sheet (g/cm^3) (*2)
Example 6	good	0.53
Comparative Example 7	poor	0.85

*1: The surface roughness of foamed rubber sheet was visually inspected.
*2: determined with a high-precision Electronic Densimeter (SD-200L, produced by Mirage Trading Co., Ltd.)

[0089] The thermo-expansive microspheres of the present invention have a narrow range of particle size distribution and superior expanding performance. Therefore the foamed rubber sheet produced with the thermo-expansive microspheres has good surface finish and light weight owing to the effective function of the thermo-expansive microspheres.

Example 7

[0090] Five weight percent of the expanded hollow microspheres (with the average particle size of 120 µm, the coefficient of variation (CV) of 27 %, and the true specific gravity of 0.020 g/cc) produced by heating the thermo-expansive microspheres of Example 1, and 95 weight percent of a PVC-sol paint (with the specific gravity of 1.4 g/cm^3) were mixed and painted on a substrate. Then the coated substrate was heated for gelling the mixed paint in a Perfect Oven at 150 °C for 30 minutes to process the coated substrate into a sheet. The result is shown in Table 2.

Comparative Example 8

[0091] A sheet was produced in the same manner as in Example 7, except that the expanded hollow microspheres (with the average particle size of 36 µm, the coefficient of variation (CV) of 41 %, and the true specific gravity of 0.172 g/cc) produced by heating the thermo-expansive microspheres of Comparative Example 4 instead of the thermo-expansive microspheres of Example 1 were employed. The result is shown in Table 2.

Table 2

	Surface finish of PVC sheet (*1)	Specific gravity of PVC sheet (g/cm^3) (*2)
Example 7	good	0.32
Comparative Example 8	poor	0.94

*1: The surface roughness of acrylic sheet was visually inspected.
*2: determined with a high-precision Electronic Densimeter (SD-200L, produced by Mirage Trading Co., Ltd.)

Example 8

[0092] A balloon was filled with 50 g of the expanded hollow microspheres (with the average particle size of 120 µm, the coefficient of variation (CV) of 27 %, and the true specific gravity of 0.020 g/cc) produced by heating the thermo-

expansive microspheres of Example 1, instead of the air, and was expanded to a volume of 4 liter. The balloon was stored at 50 °C for 1 month, but the volume did not decrease.

Claims

1. Thermo-expansive microspheres, which are **characterized by** comprising thermoplastic resinous shell and a blowing agent encapsulated in the shell, wherein the blowing agent is a fluorine-containing C_{2-10} compound of ether structure free of chlorine and bromine atoms and gasified at a temperature not higher than the softening point of the thermoplastic resin.

2. The thermo-expansive microspheres according to Claim 1, wherein the blowing agent further contains other compounds being different from the fluorine-containing compound.

3. The thermo-expansive microspheres according to Claim 1, wherein the blowing agent forms 2 to 85 weight percent of the thermo-expansive microspheres.

4. The thermo-expansive microspheres according to any one of Claims 1 to 3, which have an average particle size ranging from 1 to 100 µm and a coefficient of variation (CV), of particle size distribution being 30 % or less.

5. The thermo-expansive microspheres according to any one of Claims 1 to 4, wherein the thermoplastic resin comprises a polymer of monomeric mixture containing 80 weight percent or more of a nitrile monomer and 0.01 to 5 weight percent of a polymerizable monomer having at least two polymerizable double bonds.

6. The thermo-expansive microspheres according to any one of Claims 1 to 5, of which the surface is coated with 0.1 to 95 weight percent, based on the thermo-expansive microspheres, of a fine-particle filler having a primary particle size not larger than one tenth of the particle sizes of the thermo-expansive microspheres.

7. Expanded hollow microspheres produced by heating the thermo-expansive microspheres according to any one of Claims 1 to 6 at a temperature not lower than the softening point of the thermoplastic resinous shell to expand to a volume with 10 or more of expansion coefficient, and **characterized by** having a true specific gravity of 0.1 g/cc or lower and a particle size distribution with a coefficient of variation (CV), of 30 % or less.

8. Production process of thermo-expansive microspheres wherein at least one polymerizable monomer is polymerized in an aqueous suspension in the presence of a blowing agent, being **characterized by** the blowing agent which is a fluorine-containing C_{2-10} compound of ether structure free of chlorine and bromine atoms.

9. The production process according to Claim 8, wherein the blowing agent further contains other compounds being different from the fluorine-containing compound.

10. Foamed composition produced by blending rubber, thermoplastic resin or thermo-setting resin with 0.5 to 50 weight percent of the thermo-expansive microspheres according to any one of Claims 1 to 6, and by heating to expand the thermo-expansive microspheres.

11. Lightweight resin composition produced by blending rubber, thermoplastic resin or thermo-setting resin with 0.5 to 50 weight percent of the expanded hollow microspheres according to Claim 7.

12. Process for applying the expanded hollow microspheres according to Claim 7 as the volume-retaining materials for pressure vessels.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] C09K3/00, C08J9/32, B01J13/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] C09K3/00, C08J9/32, B01J13/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CA, REGISTRY(STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1268272 A1 (Kureha Chemical Industry Co., Ltd.), 15 January, 2002 (15.01.02), Claims 1, 2, 5, 11 to 15, 18 to 20; Par. Nos. [0002] to [0009], [0028], [0029], [0031], [0038], [064], [0087], [0090], [0097], [0098], [0100], [0101], [0103], [0107] & US 2003/114546 A1 & JP 2002-12693 A	1-12
Y	JP 11-269343 A (Inoac Corp.), 05 October, 1999 (05.10.99), Claim 2; Par. No. [0010] (Family: none)	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 April, 2004 (01.04.04)	20 April, 2004 (20.04.04)
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